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Microstructure in a biointerface

F. SONG, X. H. ZHANG, Y. L. BAI
LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
E-mail: songf@lnm.imech.ac.cn

The study of the microstructure of nacre has not yet reached maturity [1, 2]. Abalone nacre is traditionally considered as tablet-reinforced composite with a microstructure of "brick and mortar" (BM) arrangement, where bricks refer to flat polygonal crystals of aragonite and the mortar is organic adhesive composed of polysaccharide and protein fibers [3]. Recently, Schaffer *et al*. [1] observed many nanopores in the interlameller organic matrix layer of nacre, and proposed that interlamellar organic matrix delineates the aragonite tablets but allows the tablets to grow mineral bridges through the nanopores. Based on the mineral bridges, continuous growth of aragonite crystals forms abalone nacre. However, they did not give conclusive evidence of mineral bridges. With the development of high-performance materials, much attention has been given to the microstructure of biomaterials [4, 5]. In particular, nacre, which has elaborate microstructure [1, 2] and a fracture-toughness 3000 times greater than that of the pure mineral [3], has been widely investigated [1–12]. However, neither the microstructure nor the toughening mechanism of nacre is well understood [6–9]. It is generally believed that the BM arrangement of nacre results in the high performance [3, 6, 7], yet the present synthetic biomimetic materials with BM structure do not have the toughness comparable to that of nacre [9, 10]. Here we show the existence of mineral bridges and give the geometrical characteristics of mineral bridges in the organic matrix interface of nacre.

To reveal the microstructure of nacre, the samples of abalone nacre were examined by an H-8100 TEM at an accelerating voltage of 200 kV. The testing samples were the nacre from *Haliotis iris* shell (abalone shell from New Zealand), which may be varied as ceramic composites containing 9 vol% of interlocking aragonite tablets staggered in successive laminae and separated by a 5% organic matrix. The keratin layer of the shell was mechanically worn off and the nacre of the shell was washed with distilled water and air dried at room temperature. Thin films parallel to the cross sectional surface were cut with a diamond saw, mechanically sliced and ground, then thin ion-beam milled at an angle of 10° to 50 μm thickness, and finally perforated under a voltage of 5.5 kV.

The cross sectional microstructure morphology of nacre reveals an aptitude for traditional BM arrangement (Fig. 1a). However, there also exists many mineral bridges in the interlamellar organic matrix layers (Fig. 1b). The mineral bridges appear to be circular columns and their positions are random. The diameter of mineral bridges is 38–54 nm. And the height of mineral bridges is equal to the thickness of the organic matrix layer, 25–33 nm. Moreover, the thickness of an aragonite tablet on the cross sectional surface is 0.37–0.43 μm.

To obtain the structural characteristics of mineral bridges in the interlamellar organic matrix layers of nacre, first, we randomly chose some cross sectional surfaces from the sample of nacre, and counted the perfect tablets on the surfaces, namely 16 tablets. By measuring the length of these tablets on the cross sectional surfaces, we found that the average length approximately equals 4 μm (Fig. 2a). Secondly, by counting the bridges on each of the chosen tablets, we obtain that total number of bridges was 650 and have the average number on each tablet is approximately 41 (Fig. 2b). Since the microstructure of nacre can be considered to be transverse isotropic, the average bridge-to-bridge spacing and density of mineral bridges is approximately given as 98 nm and 100 μm^{-2}, respectively. Finally, we divide each of the chosen tablets into sixteen equal units along the direction of organic layer, then separately add up the number of bridges (on all chosen tablets) contained by each unit. A distribution of mineral bridges on the tablets can be given (Fig. 2c). Since the average value and standard deviation of the distribution are approximately equal to 8 and 2.6, respectively, the distribution reveals a central feature. The bridges are mainly concentrated in the central region of each tablet where the number of mineral bridges is about 70% of that on the whole tablet, and the diameter of the central region is approximately equal to 1/3 the length of the whole tablet (Fig. 1c).

In addition, the surface area of organic matrix on one side of a tablet is estimated to be approximately 16 μm^2 while the total cross sectional area of the mineral bridges in the organic matrix is about 2.7 μm^2. The area of the bridges is approximately equal to 1/6 that of the organic matrix. So nacre can be seen as a tablet-reinforced composite, whereas, its organic matrix layer itself can be considered as a fiber-reinforced composite in which the matrix is organic and the fibers are mineral bridges (Fig. 1c). We take the Young's modulus of the mineral bridges and the organic matrix as $E_b = 100$ GPa and $E_o =$ 4GPa, respectively [6], and the volume fractions of the fiber and the matrix of the organic matrix layers as $V_b = 1/6$ and $V_o = 5/6$, respectively. According to composite theory, we can estimate the Young's modulus of the organic layer as

$$\frac{E_c}{E_o} = V_b \frac{E_b}{E_o} + V_o = 5$$

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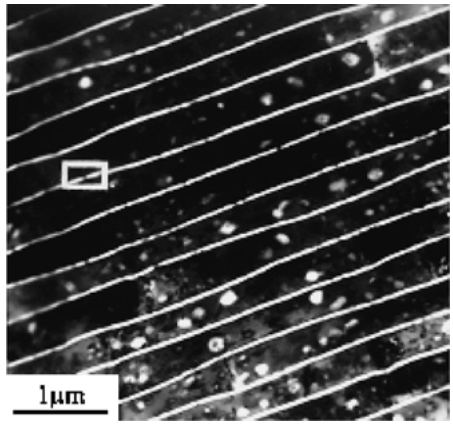
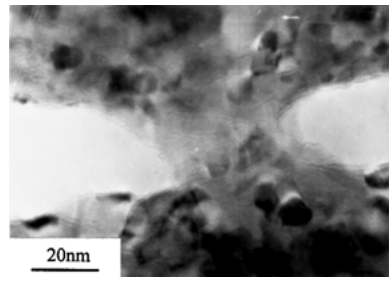


(a)



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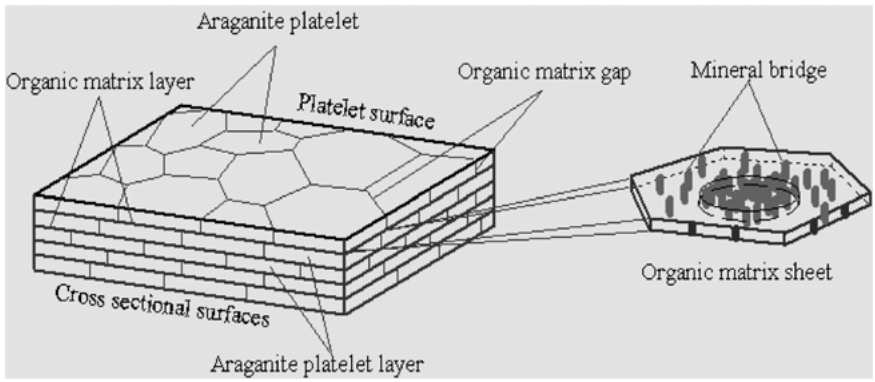
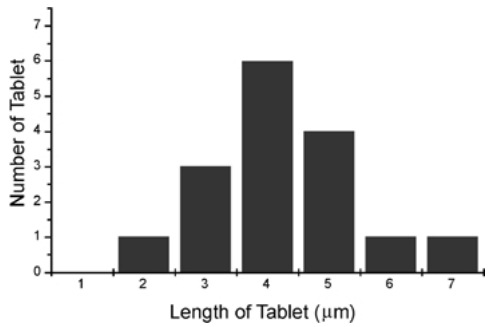
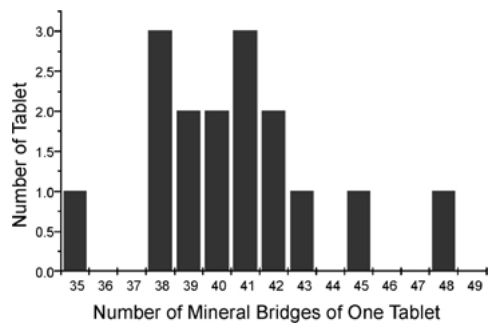


(c)

Figure 1 Transmission electron micrographs of a nacre from *Haliotis iris* shell showing the microstructure and a mineral bridge between aragonite platelet layers. (a) TEM image of the cross sectional microstructure of nacre, showing a normal lamellar structure. (b) TEM image of a mineral bridge of nacre (the boxed area in Fig. 1a). (c) Schematic illustration showing the microstructure of nacre, and the microstructure in the interlamellar organic matrix sheet which can be considered as a fiber-reinforced composite, i.e., the matrix is organic and fibers are the mineral bridges.



(a)



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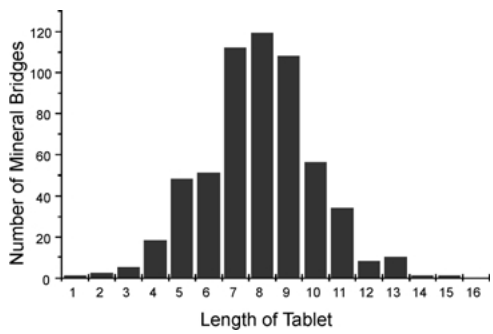

(c)

Figure 2 (a) Histogram of the measured length of 16 perfect tablets on the cross sectional surfaces. This distribution gives the average length of a tablet on the cross sectional surfaces as approximately equal to 4 μm. (b) Histogram of the measured number of mineral bridges of each of 16 tablets on the cross sectional surfaces. It shows that the average number of mineral bridges in each tablet on the cross sectional surfaces is approximately equal to 41. (c) Histogram of the distribution of the number of mineral bridges along the length of tablet on the cross sectional surfaces. The distribution reveals that most mineral bridges are concentrated on a central region of the tablet. The length of the central region is approximately equal to 1/3 the length of the tablet.

where E_c is the Young's modulus of the fiber-reinforced composite in the direction of the mineral bridges. If we do not consider the existence of mineral bridges, i.e. $V_o = 1$ and $V_b = 0$, then $E_c = E_o$, the equation becomes the traditional model of nacre. This is an indication that the mineral bridges increase the Young's modulus of organic matrix interface in the direction of the mineral bridges by five times. Obviously, mineral bridges can effectively enhance the mechanical properties of the organic matrix layers of nacre.

Nacre is, from the viewpoint of biomimetic design, an ideal composite. Its elaborate microstructure determines the outstanding mechanical behaviors of itself. And according to analyses above, the microstructure of nacre should be referred to as a "brick-bridge-mortar" (BBM) structure instead of traditional "brick-mortar" one. In addition, the crystallographic orientations of 3–10 successive tablets remain the same [12], so it is reasonable to suggest the microstructure of nacre as a slightly tangled BBM structure.

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